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FACILE SYNTHESIS OF Pd NANOPARTICLES ON SILICA SUPPORTS AS RECYCLABLE CATALYSTS FOR SUZUKI-MIYAURA REACTION IN WATER: EFFECT OF DONOR LIGANDS

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Abstract: Silica supported palladium nanoparticles (PdNPs) were prepared by a convenient one-step method, without taking assistance from any external reductant or stabilizer. The ligands (-NMe_2, -NH_2 and –SH) anchored to silica gel play the dual role of reducing and stabilizing agent. The materials were characterized by techniques such as N_2 adsorption-desorption, HR-TEM, ICP and XRD analyses and applied as catalysts for Suzuki-Miyaura coupling of aryl bromides in water. With the catalysts (PdNP-NMe_2@SiO_2 and PdNP-NH_2@SiO_2) coupling reactions aryl bromides were performed without using any phase transfer additive. Under similar experimental conditions, catalyst PdNP-NMe_2@SiO_2 shows better activity than other systems. The catalysts could be reused at least six cycles without significant loss in their activity. TEM images show no aggregation of NPs even after reusing the catalysts for six times.

Keywords: Palladium nanoparticles; N-ligand; heterogeneous catalyst; Suzuki-coupling; water; aryl bromide

1. Introduction:

The compounds containing biaryl moiety are known to have tremendous applications in synthesis of various biologically and pharmaceutically essential molecules. Among the various methods, palladium catalyzed Suzuki-Miyaura coupling of similar/dissimilar Csp^2-Csp^2 fragments by reacting organo-halides and organo boronic acids remains extremely popular technique for synthesis of such organic compounds [1, 2]. Historically, ligand-based molecular catalysts have proven to be very effective for such type of Suzuki-Miyaura reactions. But from economical and environmental perspectives, these molecular catalysts are least preferred due to their difficulties in recovery and recycling [3]. Nanoparticles (NPs) either in their colloidal form or supported on solids are one of the most valuable alternatives to these molecular catalysts in recent times [4]. Supported metal NPs are more preferred than colloidal NPs because of their easy separations and better recycling properties. Among the various solid support materials for PdNPs such as silica [5], MCM-41 [6], SBA-15 [7], MOF [8] *etc.* to design efficient heterogeneous catalysts, silica is considered to be the best choice because of its easy accessibility, economic viability, excellent porosity, and easy surface modification capability.

Although there are several methods of synthesizing NPs, the one using reducing and capping agent to transform Pd^{II} salt to stable Pd^0 species is most common. Numerous Pd nanocatalysts are known in which the PdNPs are stabilized by use of donor ligands like phosphines [9], thiols [10], pyrazole [11], *etc.* Out of these various donor atoms, phosphine based ligands are widely investigated for obtaining efficient stable nanocatlysts for Suzuki reactions. In our earlier work [12], we have demonstrated that the supported phosphine ligand could conveniently reduce a Pd^{II} centre and at the same time stabilize the resulting NPs. Although this method of using phosphine ligand for generating PdNPs, represents one of the most simple and effective methods that can eliminate the use of harmful reductant and stabilizer in NPs synthesis, the high cost together with toxicity and air sensitive property of the phosphine poses a limit to the catalytic system. Thus, it is of great importance to develop new methods for synthesizing supported PdNPs with relatively uniform particle size distribution preferably under phosphine-free conditions.

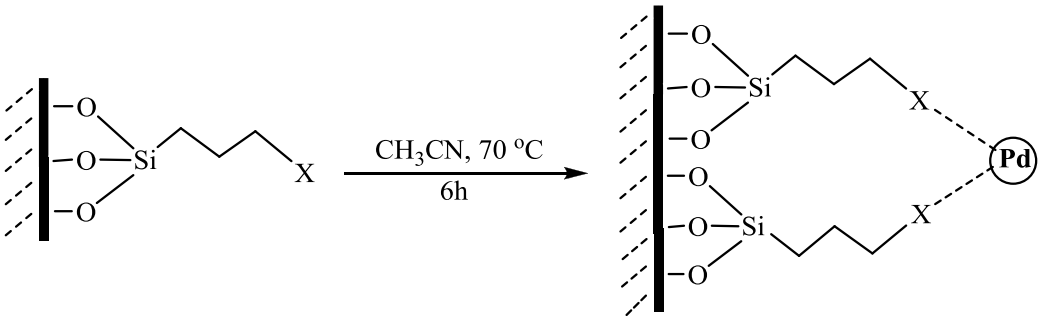
In this context, we synthesized three palladium nanocatalysts by using $PdCl_2$ and silica supported nitrogen and thiol based ligands without using any external reductant or stabilizer. The catalysts have been employed for the

Suzuki-Miyaura reaction of aryl bromides in water. It may be noted that although significant efforts have been devoted nowadays to explore aqueous condition in Suzuki reactions, however, most of the successful systems are still homogeneous in nature [13,14]. Except few novel examples [15,16], majority of the reported heterogeneous Pd-catalysts often fail to activate aryl halides as substrates in water. As from the cost and environmental point of view water is the most deserving solvent for any organic reactions, therefore, development of new heterogeneous Pd catalysts for effective activations of aryl halides in water is one of the most attractive areas of research.

2. Results and discussion:

2.1. Synthesis of the catalysts:

The palladium catalysts PdNP-NMe_2@SiO_2, PdNP-NH_2@SiO_2 and PdNP-SH@SiO_2 were synthesized by a simple one-step reaction between $PdCl_2$ and commercially available 3-dimethylaminopropyl functionalized silica gel (NMe_2@SiO_2), 3-aminopropyl functionalized silica gel (NH_2@SiO_2) and 3-mercaptopropyl functionalized silica gel (SH@SiO_2) (Scheme 1).



X = NMe_2; **PdNP-NMe_2@SiO_2**
= NH_2; **PdNP-NH_2@SiO_2**
= SH; **PdNP-SH@SiO_2**

Scheme 1: Synthesis of the silica supported palladium catalysts.

2.2. Characterization of the catalysts:

HRTEM analysis:

From the TEM images of the catalysts (Fig. 1) it can be seen that the synthetic protocols for generation of PdNPs without employing any reducing and stabilizing agent, worked effectively for PdNP-NMe_2@SiO_2 and PdNP-NH_2@SiO_2. However, under similar experimental condition, the procedure failed for the system with SH@SiO_2. The HR-TEM image as well as the SAED pattern clearly suggests the absence of any NPs formation in PdNP-SH@SiO_2 (Fig. 2)

The TEM images of the catalysts, PdNP-NMe_2@SiO_2 and PdNP-NH_2@SiO_2 recorded at 50nm showed that the nano-sized Pd particles are evenly dispersed across the silica support (Fig. 1a and 1c). The majorities of the Pd-NPs are in the range 3-6 nm and are in spherical or elliptical

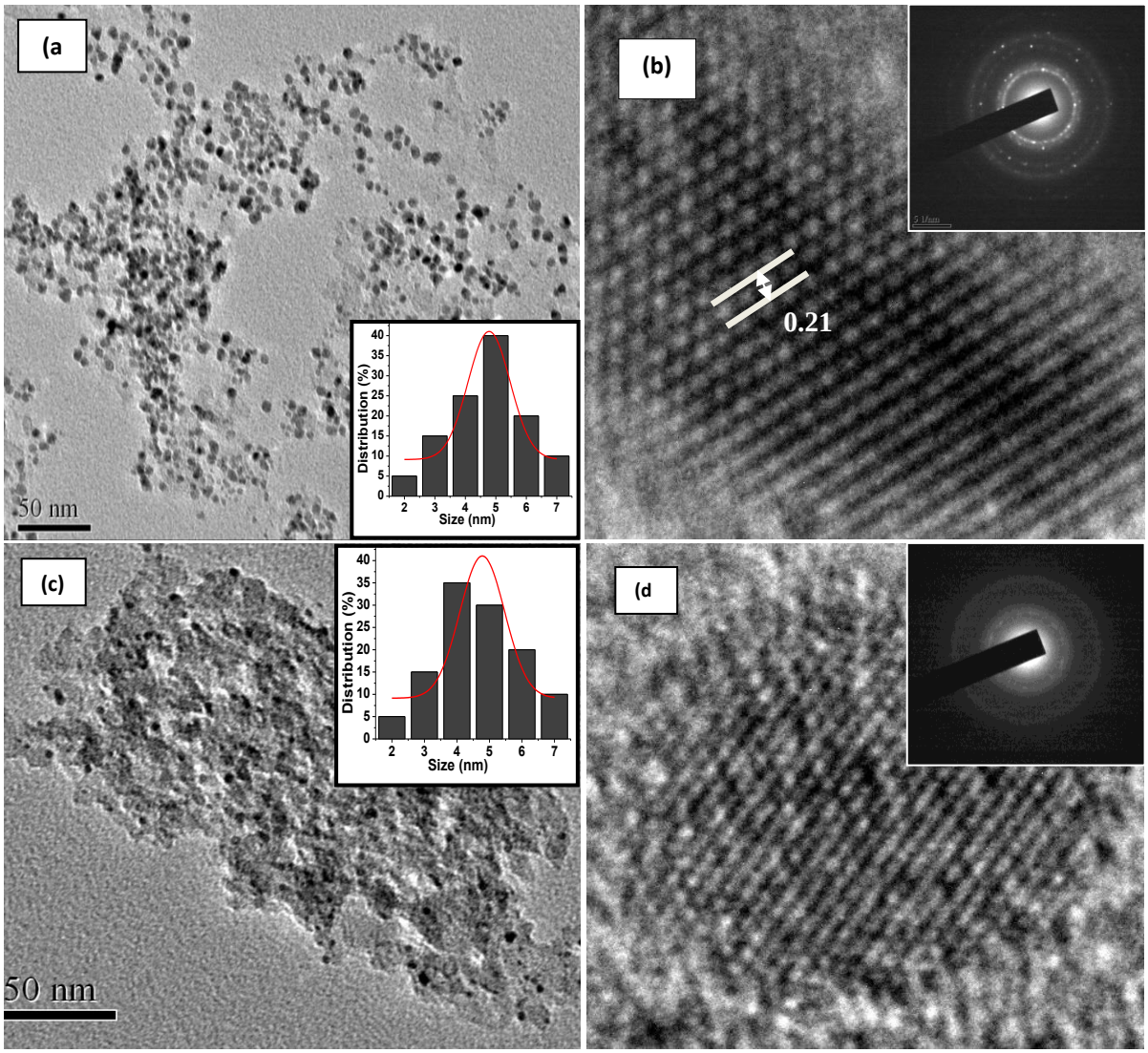


Figure 1: (a) TEM micrographs of PdNP-NMe_2@SiO_2 and particle size histograms with a Gaussian curve fitting (inset) and (b) HRTEM image and SAED pattern (inset) of PdNP-NMe_2@SiO_2. (c) TEM micrographs of PdNP-NH_2@SiO_2 and (d) HRTEM image of PdNP-NH_2@SiO_2.

in shape. The crystalline nature of the NPs in PdNP-NMe_2@SiO_2 and PdNP-NH_2@SiO_2 was evident from the selected area electron diffraction (SAED) pattern which showed a fringe width of about 0.21 nm consistent with the face centre cubic (fcc) arrangement of the nanocrystals (**Fig. 1b** and **1d**) **[17]**.

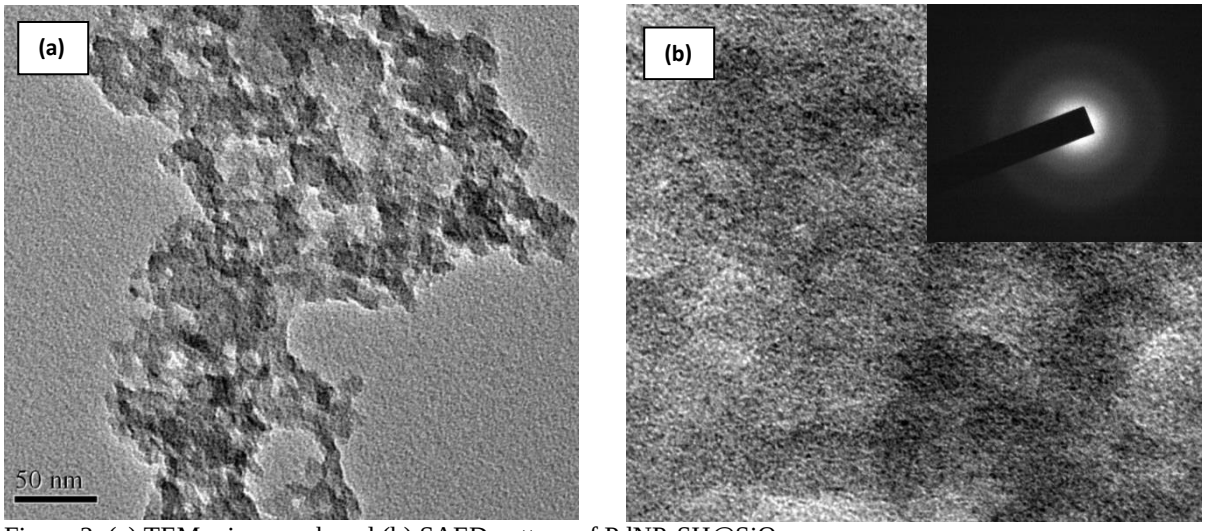


Figure 2: (a) TEM micrograph and (b) SAED pattern of PdNP-SH@SiO_2.

BET surface and ICP analysis:

The N_2-adsorption-desorption isotherm of the catalysts PdNP-NMe_2@SiO_2 and PdNP-NH_2@SiO_2 displays a *type IV* isotherm corresponding to the mesoporous nature of the silica based supports (Fig. 3) [18]. The respective textural parameters, such as the specific surface area, the pore volume and pore diameters are presented in Table 1. The specific surface area of the catalysts showed a gradual decrease in its value compared to that of the metal free support which is consistent with successful immobilization of palladium onto the silica mesopores. In a similar manner, a gradual decrease in pore volume and pore diameter in the catalysts further substantiates the immobilization. The palladium loading determined using ICP-AES technique gave the value 0.39 $mmolg^{-1}$ and 0.33 $mmolg^{-1}$ of silica gel for PdNP-NMe_2@SiO_2 and PdNP-NH_2@SiO_2.

Table 1: Textural data of the catalysts and support materials determined by BET method.

Material	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
NMe_2@SiO_2	438	0.47	5.77
PdNP-NMe_2@SiO_2	328	0.46	5.51
NH_2@SiO_2	416	0.65	6.33
PdNP-NH_2@SiO_2	308	0.59	5.87

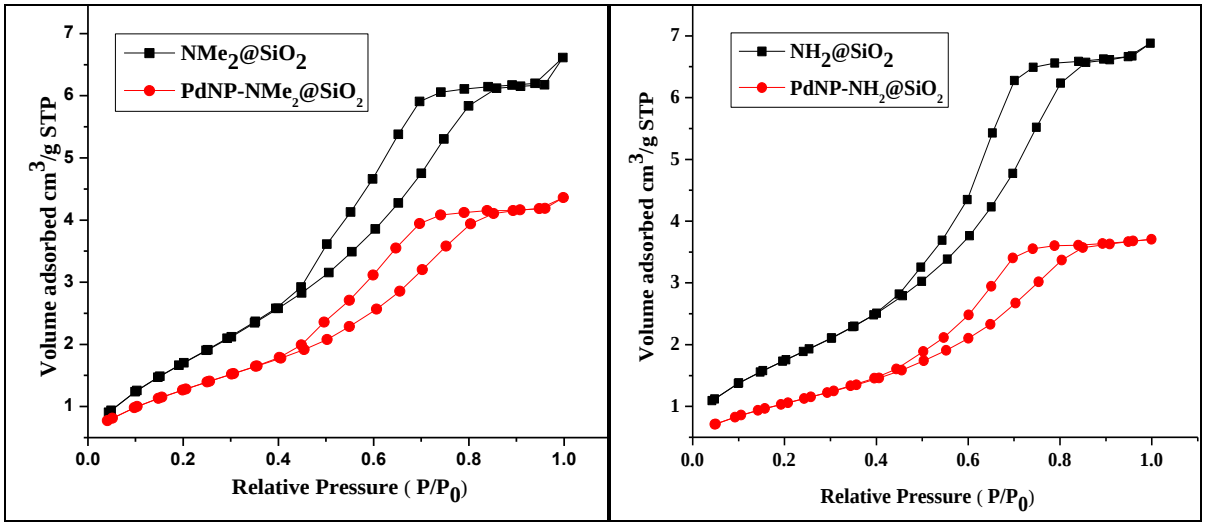


Figure 3: N_2 adsorption-desorption isotherms of PdNP-NMe_2@SiO_2 and PdNP-NH_2@SiO_2.

SEM-EDX analysis:

The SEM image for the catalysts PdNP-NMe_2@SiO_2 (**Fig. 4a**) and PdNP-NH_2@SiO_2 (**Fig. 4b**) shows the morphology and dimension of the silica gel. Although palladium is not clearly visible from the images, the presence of Pd peak in the respective EDX spectra confirms their existence in the silica matrix of the catalysts.

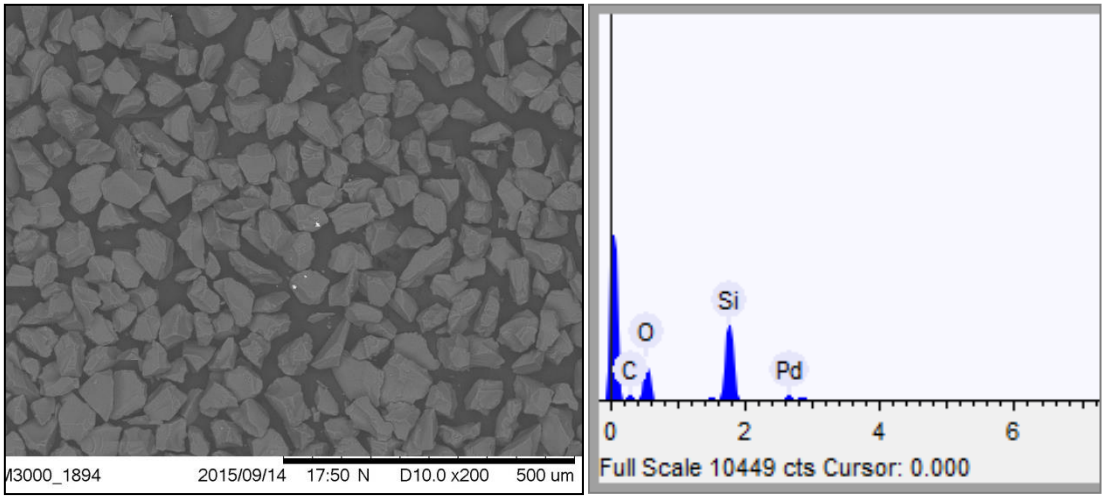


Figure 4: (a) SEM-EDX spectra of the catalysts PdNP-NMe_2@SiO_2.

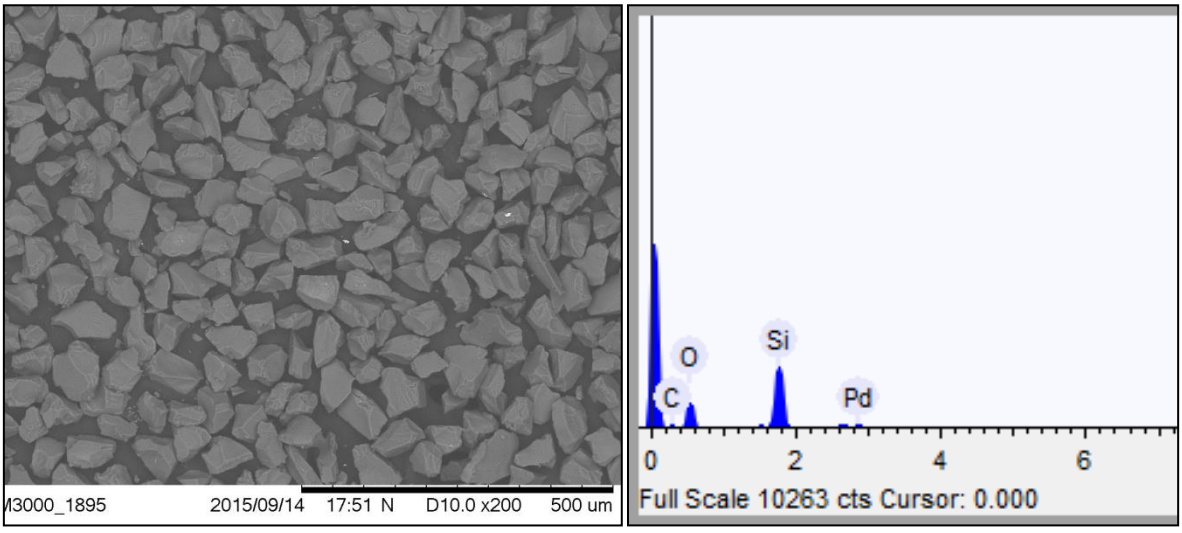


Figure 4: (b) SEM-EDX spectra of the catalysts PdNP-NH_2@SiO_2.

XRD analysis:

The powder XRD patterns (Fig. 5) of PdNP-NMe_2@SiO_2 showed a broad peak for silica at $2\theta = 22.4^o$. In addition four other low intensity diffraction peaks at (111), (200), (220) and (311) planes were also visible; corresponding to Pd^0 nanocrystals (JCPDS card No. 001-1201).

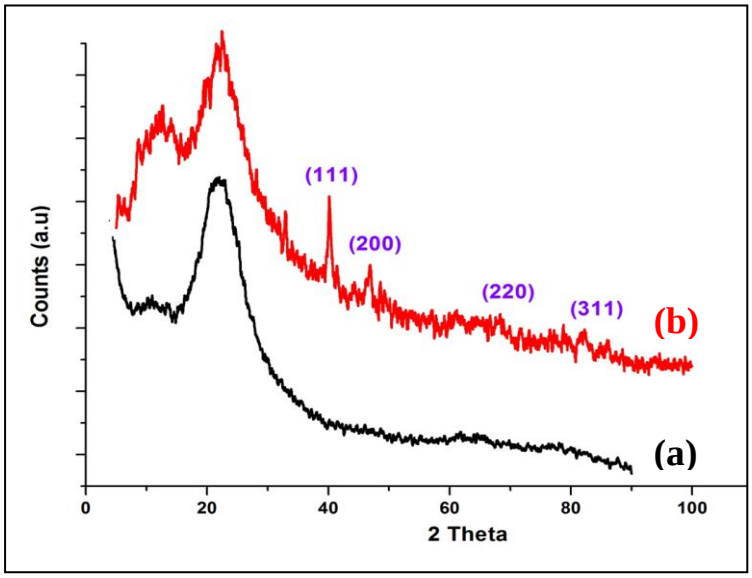


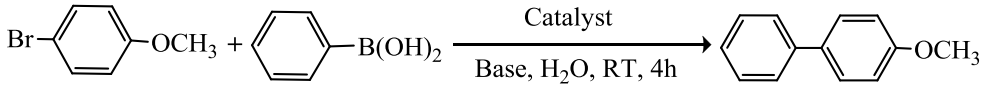
Figure 5: Powder XRD patterns of (a) $NMe_2@SiO_2$ and (b) $PdNP\text{-}NMe_2@SiO_2$.

2.3. Catalytic studies:

Optimization studies for aryl bromides:

The activities of catalysts $PdNP\text{-}NMe_2@SiO_2$ and $PdNP\text{-}NH_2@SiO_2$ were examined in the Suzuki–Miyaura reaction of aryl bromides employing *p*-bromoanisole and phenylboronic acid as model substrates using water as solvent and K_2CO_3 as base (Table 2). With 0.5 mol% catalyst, we are delighted to see that the coupling reaction proceeded smoothly in water at room temperature and, almost quantitative conversion was obtained (entries 1 and 2). In a controlled experiment, when the same reaction was performed with homogeneous $PdCl_2$ salt as catalyst without using the supported ligand, only 44% conversation was obtained (entry 3). The superior performance of the catalysts over homogeneous $PdCl_2$ could be attributed to the cooperative influence with the amine ligand functionalized onto silica gel. It may be noted that numerous examples of cooperative catalysis by silica-based heterogeneous materials for various organic reactions have been already reported [19, 20]. Among other bases, our catalysts afforded maximum yield with K_2CO_3. On varying the catalyst quantity to 0.1 mol%, it was observed that product yield with $PdNP\text{-}NMe_2@SiO_2$ remain unchanged, whereas there is a dramatic decrease in biphenyl formation with $PdNP\text{-}NH_2@SiO_2$ (entry 12 vs 13). Thus the optimal catalyst quantity for the Suzuki–Miyaura reaction was chosen to be 0.1 mol% and subsequently all other reactions were performed at these optimized conditions (entry 12).

Table 2. Optimization of base and catalyst quantity for Suzuki-Miyaura cross coupling of p-bromoanisole with phenylboronic acid[a]



Entry	Catalyst	Base	Catalyst (mol%)	Yield (%)[b]
1	$PdNP\text{-}NMe_2@SiO_2$	K_2CO_3	0.5	98
2	$PdNP\text{-}NH_2@SiO_2$	K_2CO_3	0.5	97
3	$PdCl_2$	K_2CO_3	0.5	44
4	$PdNP\text{-}NMe_2@SiO_2$	Cs_2CO_3	0.5	96
5	$PdNP\text{-}NH_2@SiO_2$	Cs_2CO_3	0.5	92

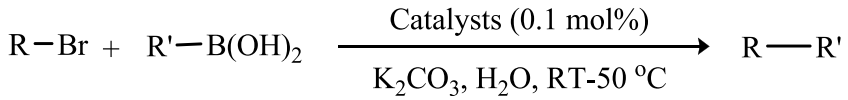
6	PdNP-NMe_2@SiO_2	NaOH	0.5	88
7	PdNP-NH_2@SiO_2	NaOH	0.5	85
8	PdNP-NMe_2@SiO_2	Na_2CO_3	0.5	84
9	PdNP-NH_2@SiO_2	Na_2CO_3	0.5	86
10	PdNP-NMe_2@SiO_2	K_2CO_3	0.2	98
11	PdNP-NH_2@SiO_2	K_2CO_3	0.2	91
12	PdNP-NMe_2@SiO_2	K_2CO_3	0.1	98
13	PdNP-NH_2@SiO_2	K_2CO_3	0.1	83
14	PdNP-NMe_2@SiO_2	K_2CO_3	0.05	82
15	PdNP-NH_2@SiO_2	K_2CO_3	0.05	67

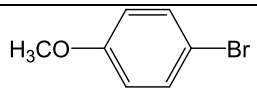
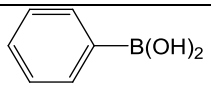
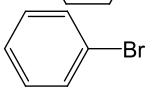
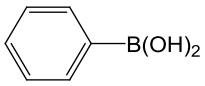
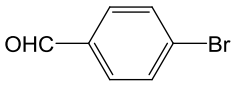
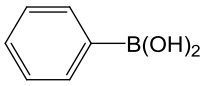
[a]Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.65 mmol), base (1.5 mmol), H_2O (6 mL), 4 h; [b]Isolated yields.

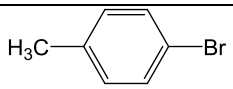
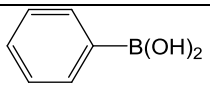
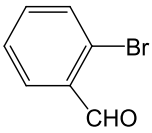
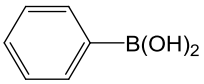
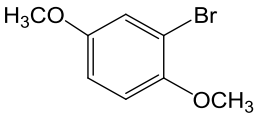
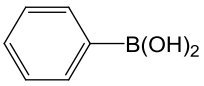
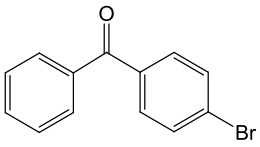
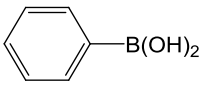
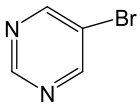
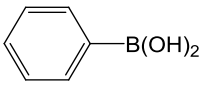
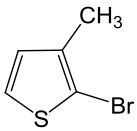
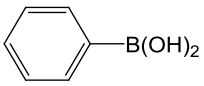
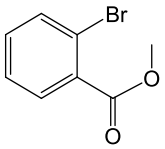
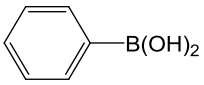
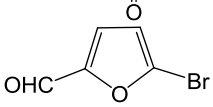
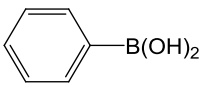
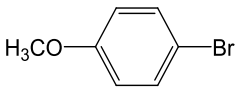
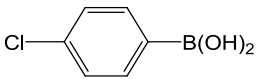
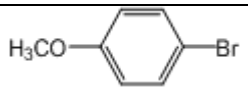
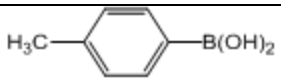
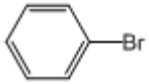
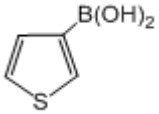
Effects of aryl/heteroaryl bromides as substrates:

With our initial optimization study, we extended the applicability of the catalysts for a range of sterically and electronically different aryl bromides (Table 3). It was seen that dimethyl aminopropyl supported catalyst PdNP-NMe_2@SiO_2 afforded better yields than their APTES counterpart PdNP-NH_2@SiO_2 which can be attributed to the better stabilizing nature of the tertiary amine donor ligands than the primary amine. With PdNP-NMe_2@SiO_2 good-to-excellent yields of cross-coupling products were obtained in most of the cases (Table 8). Efficient cross-coupling activities were also obtained with hindered *ortho*-substituted aryl halides like, 2-bromobenzaldehyde (entry 5) or 1-bromo-2,5-dimethoxybenzene (entry 6). Interestingly, biaryls containing heterocyclic groups, which are usually considered as the testing grounds for cross-coupling reactions were also accessible by our catalytic systems under slightly warm conditions (entries 8, 9 and 11). It may also be noted that changing the boronic acid from phenyl to tolyl (entry 13) / chloro (entry 12) had very little influence in our catalytic system. However hetrocyclic boronic acid such as 2-thienylboronic acid gave relatively low yield (entry 14).

Table 3: Suzuki-Miyaura cross coupling reactions of aryl/heteroaryl bromides with arylboronic acids using catalysts PdNP-NMe_2@SiO_2 and PdNP-NH_2@SiO_2[a].



Entry	R-Br	R'-$B(OH)_2$	Time (h)	Yield (%)[b,c]	
				PdNP-NMe_2@SiO_2	PdNP-NH_2@SiO_2
1			4	98	83
2			4	97	89
3			4	85	68

4			4	96	86
5			6	80	62
6			6	87	79
7			6	83	77
8			8	82[c]	58[c]
9			8	80[c]	63[c]
10			8	86[c]	67[c]
11			8	76[c]	55[c]
12			7	88	83
13			7	92	87
14			8	63[c]	47[c]

[a]Reaction conditions: aryl bromide (0.5 mmol), arylboronic acid (0.65 mmol), K_2CO_3 (1.5 mmol), H_2O (6mL); [b]Isolated yields;
[c]Reactions are conducted at 50 ^oC.

Reusability test:

Reusability of the catalysts PdNP-NMe_2@SiO_2 and PdNP-NH_2@SiO_2 were performed with our model system taking *p*-bromoanisole and phenylboronic acid in water. After each run the catalysts were recovered by simple filtration washed thoroughly with ^{i}PrOH-H_2O (1:1), dried at 100 ^oC for 8 h and then used for subsequent runs.

Both the catalysts were found to be recyclable atleast six times without any significant drop in their activity (Fig. 6). The ICP-AES analysis of the 6th time used catalysts shows only negligible loss in Pd content (< 2%).

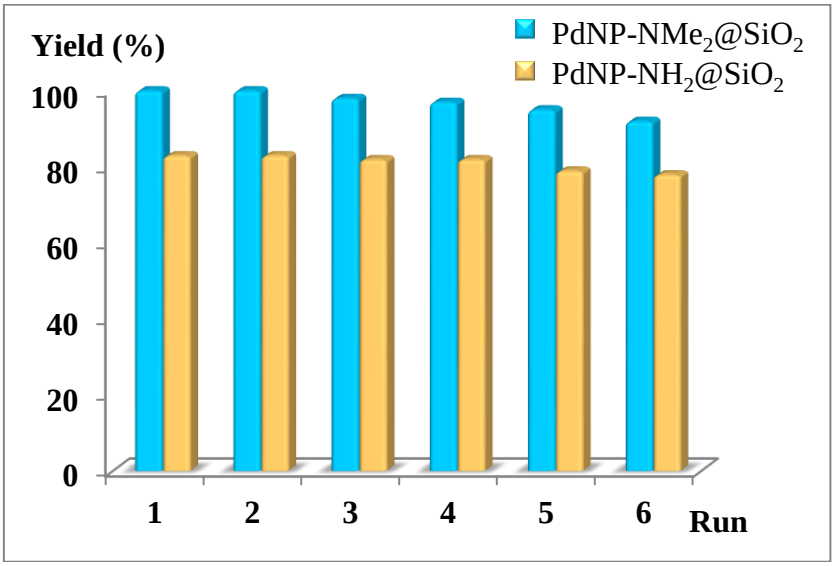


Figure 6: Bar diagram showing the recyclability of the Suzuki-Miyaura cross coupling of p-bromoanisole with phenylboronic acid using catalysts PdNP-NMe_2@SiO_2 and PdNP-NH_2@SiO_2.

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Heterogeneity test:

In order to further evaluate the contribution of any Pd leaching from the support to product formation, hot-filtration test (Fig. 7) along with solid phase poisoning test were performed with the model reaction. No decrease in the product yield confirms that the catalysts are truly heterogeneous in nature.

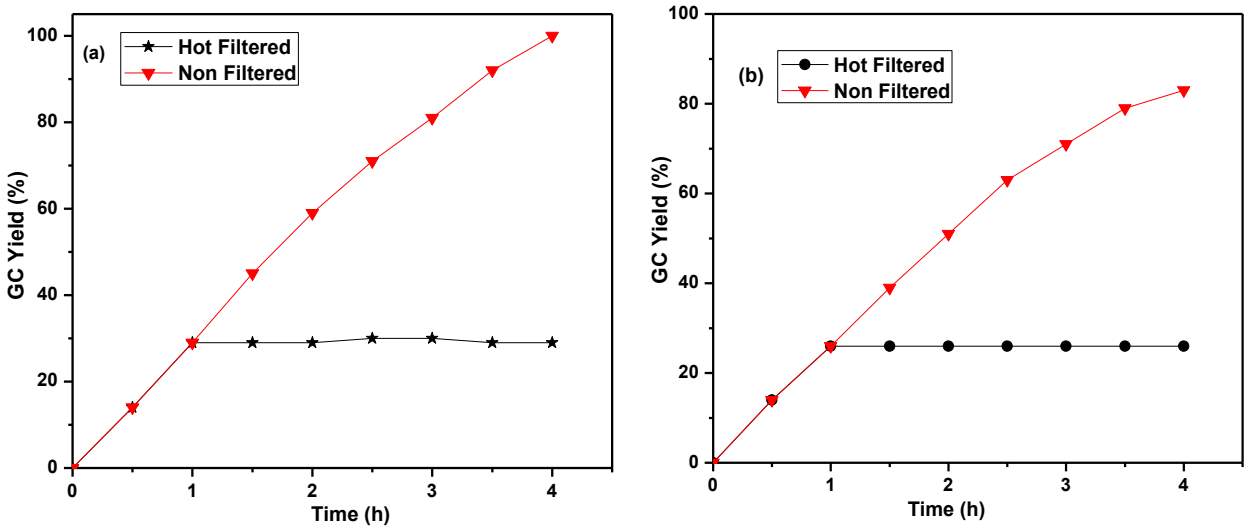

Figure 7: Hot filtration test for the coupling reaction between p-bromoanisole and phenylboronic acid using (a) PdNP-NMe_2@SiO_2 and (b) PdNP-NH_2@SiO_2 as catalyst.

3. Conclusion:

We have demonstrated a convenient protocol for synthesis of three phosphine-free silica-supported Pd nanocatalysts, without using any external reducing or stabilizing agent. The nanocatalyst PdNP-NMe_2@SiO_2 could efficiently catalyze the Suzuki coupling of aryl bromides in water at room temperature. The catalyst could be recycled several times without compromising with its activity. The facile synthesis of the catalyst combined with high product yields at relatively mild condition is the main advantages of the silica supported heterogeneous system.

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